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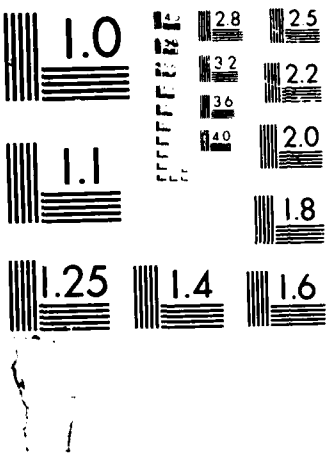
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FOREIGN TECHNOLOGY DIVISION

HIGH-MOLECULAR COMPOUNDS

(Selected Articles)

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HUMAN TRANSLATION

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HIGH-MOLECULAR COMPOUNDS (Selected Articles)

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Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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COPOLYMERIZATION OF METHYLMETHACRYLATE WITH STAINED MONOMERS, PRODUCED ON A BASE OF AMINO STYRENES

A. M. Shur, A. P. DONYA

Earlier [1] we published results of a study of copolymerization of styrene with a number of stained monomers [2], which were obtained on a base of n- and m-amino styrenes. In this report we present data on copolymerization of methylmethacrylate (MMA) with the same monomer dyes, (MK) [2]: 1-n-vinylbenzeneazo-2-azothole A (I), 1-m-vinylbenzeneazo-2-azothole A (II), 1-n-vinylbenzeneazo-2-azothole PT (III), 1-m-vinylbenzeneazo-2-azothole PT (IV), 1-n-vinylbenzeneazo-2-azothole PA (V), 1-m-vinylbenzeneazo-2-azothole PA (VI), 4-vinyl-4'-diethynolaminoazobenzene (VII), 3-vinyl-4'-diethynolaminoazobenzene (VIII), n-nitrobenzylidene-n-aminostyrene (IX), m-nitrobenzylidene-n-aminostyrene (X), n-nitrobenzylidene-m-aminostyrene (XI), m-nitrobenzylidene-m-aminostyrene (XII), 4-vinyl-2', 4', 6'-trinitrodithenylamine (XIII), 3-vinyl-2', 4', 6'-trinitrodithenylamine (XIV), 4-vinyl-2', 4' -dinitrodithenylamine (XV), 3-vinyl-2', 4', -dinitrodithenylamine (XVI).

Table 1

Composition of stained copolymers of MMA*

(1) Краситель	(2) Температура полимеризации			
	70 ± 0,02°		80 ± 0,02°	
	(3) мол. вес сополимера **. $\cdot 10^{-3}$	средняя молекулярная доля красителя в молекуле сополимера (4)	(3) мол. вес сополимера **. $\cdot 10^{-3}$	средняя молекулярная доля красителя в молекуле сополимера
I	87,1	0,197	80,7	0,081
II	96,6	0,269	89,5	0,148
III	88,0	0,195	81,1	0,084
IV	97,2	0,271	89,3	0,150
V	86,3	0,196	80,3	0,084
VI	96,9	0,268	89,8	0,152
VII	95,4	0,034	90,1	0,018
VIII	104,2	0,068	97,2	0,029
IX	78,5	0,149	69,7	0,101
X	79,8	0,168	73,0	0,124
XI	96,5	0,232	88,0	0,172
XII	99,0	0,259	90,5	0,210
XIII	88,8	0,221	61,9	0,058
XIV	95,9	0,255	64,0	0,138
XV	89,8	0,231	62,3	0,105
XVI	97,0	0,261	67,7	0,159
Без красителя (5)	89,2	—	80,4	—

* Concentration of dyes in the original mixture 0.03 mole %.

** Molecular weight of copolymers were determined viscosimetrically for the values of K and alpha for PMMA at 25 ± 0.01° in acetone (K=7.5 X 10^{-5}, α=0.70).

Key: (1) Dye; (2) Polymerization temperature; (3) Molecular weight of copolymer; (4) Average molecular fraction of the dye in a molecule of copolymer; (5) With out dye.

The content of MK links in the products of copolymerization were determined, as earlier, by the colorimetric method.

As in the case of copolymerization of MK with styrene [1], the more intensely dyed copolymers of MMA are formed when using MK, which is produced on a base of m-amino styrene (Table 1). The molecular weights of the structurally dyed polymethylmethacrylates (PMMA) in

comparison with similar samples of polystyrene are slightly greater and have a tendency to increase during the transition from MK, which contain n-vinylphenol radical (I, III, V, VII, IX, X, XIII, XV), to dyes with m-vinylphenol radical (II, IV, VI, VIII, XI, XII, XIV, XVI).

Table 2

Fractionation of the copolymer of MMA with 1-n-vinyl-benzeneazo-2-azothole A* (3.0000 g of copolymer in 100 ml of acetone)

(1) Фракция, №	(2) Добавлено метанола, мл	(3) Вес фракций, г	(4) Оптическая плотность 0,5%-ных растворов фракций в ацетоне (λ 536 ммк, l 20 мм)	(5) Мол. вес·10⁻³
1	15	1,710	0,375	109,3
2	30	0,579	0,313	76,0
3	45	0,282	0,255	51,1
4	60	0,186	0,229	42,6
5	75	0,141	0,175	29,7
6	90	0,099	0,106	19,9

* The content of dye in the unfractionated colored copolymer is 0.0227 mole %; molecular weight 87 100.

Key: (1) Fraction number; (2) Added methanol, ml; (3) Weight of fractions, g; (4) Optical density of 0.5% solutions of fractions in acetone (λ 536 mmk, l is 20 mm); (5) Molecular weight 10^{-3}.

As results of fractionation of the structurally dyed PMMA reveal (Table 2), all fractions of the polymer have more or less intense tinting, and the optical density of the equally concentrated solutions of individual fractions increases with and increase of thermal molecular weight.

Experimental Part

Saturated solutions of corresponding MK in the freshly distilled MMA (boiling point 100-100.5°, n_d^{20} 1.4156) were poured into ampules (2 ml each), which contain 1% freshly recrystallized benzoyl peroxide. After removing air from the mixture of monomers by nitrogen the ampules were placed for 8 hours into a thermostat with temperature of 70 or 80°.

The resulting dyed copolymers, which were treated with methanol (10 ml), were precipitated twice from acetone (20 ml each) by methanol (100 ml each). The combined filtrates, which contain MK which do not enter into reaction, were added to 500 ml by a mixture of acetone with methanol (1:5) and were measured colorimetrically in the FEKN-57 photocolorimeter (thickness of the layer is 20 mm) under the same conditions in which the calibration graphs were made [1]; λ=536 mmk for dyes I-VI and λ=413 mmk for dyes VII-XVI. From the difference between the quantity of MK found by this method and the content of it in the original mixture we calculated the composition of the dyed copolymer.

Conclusions

1. We studied block copolymerization of methylmethacrylate with 16 monomer dyes, which were obtained on a base of n- and m-aminostyrenes.

2. It is shown that sufficiently intense structural dying of block polymethylmethacrylate is achieved by introducing 0.03 mole % of monomer dye into the original mixture.

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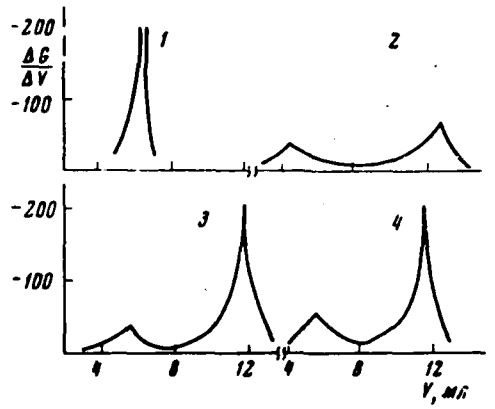
December 16, 1968

STUDY OF THE STRUCTURE OF A MACROMOLECULAR CHAIN OF COPOLYMERS OF ALPHA-CHLOROACRYLIC ACID

V. P. Barabanov, V. M. Tsentovskiy

Copolymerization of acrylic acids with different unbound compounds in the majority of cases leads to the formation of statistical copolymers with equally likely distribution of monomer links in the macromolecule [1]. But in the case of alpha halogen acrylic acids and their esters the possibility of specific ordering is assumed in the location of links [2]. The purpose of studying the structure of a macromolecular chain we used the method of potential metric titration. The objects of the study were alpha chloroacrylic acid (KhAK) in monomer, homopolymer and copolymer (with methylmethacrylate) form [3].



Curves of potential metric titration of solutions of copolymers of KhAK (molecular %): 1-1, 2-5, 3-10, 4-15.

In order to improve conditions of titration the reaction was conducted in dimethylformamide, which is a good differentiating solution with relatively high dielectric constant (36.7) [4]. As the titrating medium we used methanol solution of tetraethylammonia-hydroxide.

Results of titration are given in the figure. As one can see from the path of the curves, the clearest titration discontinuity is observed for solutions of the copolymer with 1% content of KhAK. This is evidence of the fact that the distribution of ionogenic groups is uniform in the macro molecular chain, and due to the insignificant acidity each carboxyl group manifests its individual properties. (One should note that even in a solution of monomer acid such an abrupt discontinuity is not observed due to possible association).

An increase of concentration of acid in the original reaction mixture leads to the fact that in the macro molecule which is formed it is not individual links which are statistically redistributed, but groups of links, which manifest properties of the dicarboxylic acid. This is confirmed by the presence of two discontinuities on the titration curve of copolymers with the content 5, 10 and 15% КhAK. A further increase in the content of acid in the copolymer leads to the fact that the mutual affect of adjacent carboxyl groups becomes commensurate with induction affect of the dimerized links, and the polymer begins to behave as a polybasic acid. Such a phenomenon with high density of the ionogenic groups is observed for polymers of maleic acid [5].

These data of the potentiometric titration allow one to conclude that КhAK copolymerizes with methylmethacrylate with a formation of groups of links, which manifest properties of dicarboxylic acids. The proposed method of nonaqueous titration can be used for the characteristic of the structure of macro molecular chains.

Conclusions

The method of potentiometric titration in dimethylformamide was used to study the structure of macro molecular chain of copolymers based on alpha-chloroacrylic acid and methylmethacrylate. With a content of the acid 5, 10 and 15 mole. % to discontinuities of the potential are noted on the titration curves, which is related to

statistical distribution in the macro molecule of dimerized links of the acid.

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